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ARTICLE

Additive-Free Cobalt-Catalysed Hydrogenation of Carbonates to Methanol and Alcohols

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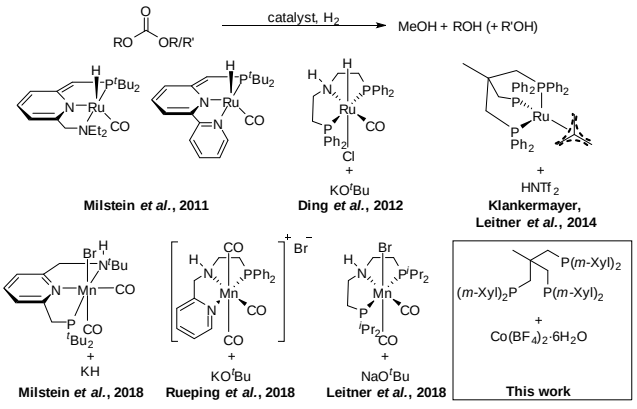
Francesco Ferretti,[a,b] Florian Korbinian Scharnagl,[a] Anna Dall'Anese,[a,c] Ralf Jackstell[a], Sarim Dastgir,[d] and Matthias Beller[a]*

Reduction of various organic carbonates to methanol and alcohols can be achieved in the presence of a molecularly-defined homogeneous cobalt catalyst. Specifically, the use of $Co(BF_4)_2$ in combination with either commercial or tailor-made tridentate phoshine ligands allows for additive-free hydrogenations of carbonates. Optimal results are obtained at relatively mild conditions (120°C, 50 bar hydrogen pressure) in the presence of xylyl-Triphos **L4**.

Introductions

The catalytic hydrogenation of carbon dioxide to methanol is of general interest in the context of the so-called "Methanol Economy". This concept comprises the capture of carbon dioxide from the atmosphere and its conversion to methanol or dimethyl ether, using dihydrogen as pointed out originally by Asinger[1] and Olah[2, 3]. Although most efforts focused on heterogeneous catalysts, also the development of suitable molecularly-defined catalysts is interesting due to the potentially higher activity. Thus in recent years, notable contributions in this area have been made by the groups of Milstein,[4] Klankermayer and Leitner,[5-7] Olah and Prakash,[8-13] Sanford,[14, 15] Himeda and Laurenczy,[16] Wass,[17] Martins and Pombeiro,[18] as well as our group.[19, 20] So far, a ruthenium-based PNP pincer complex constitutes the most productive homogeneous system with a reported turnover number (TON) of 9900, albeit after 10 days.[12] An alternative approach to the direct hydrogenation of carbon dioxide makes use of cyclic and/or acyclic organic carbonates. The former derivatives can be easily synthesised from carbon dioxide and epoxides, as already done on industrial scale in the so-called OMEGA process by Shell. The latter carbonates are mainly obtained from CO_2 by indirect methods (i.e alcoholysis of other carbon dioxide derivatives such as urea or cyclic carbonates) nowadays, but can also be directly prepared from CO_2 and alcohols. [21-23] Subsequent hydrogenation leads to methanol and the corresponding alcohols.[24] This indirect strategy for CO_2 reduction was first demonstrated by Milstein in 2011, who reported the selective hydrogenation of carbonates, carbamates and formates to methanol using different ruthenium-PNN-pincer complexes.[25-27] Later on, the use of ruthenium-based NHC-pincer systems has been described.[28, 29] The groups of Leitner and Klankermayer extensively studied [Ru(Triphos)(TMM)] (Triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane and TMM = trimethylene methane) in hydrogenations of carboxylic and carbonic acid derivatives, including cyclic and acyclic carbonates in the presence or the absence of the additive $HNTf_2$.[30] So far, the most productive catalyst for this reaction has been reported by the group of Kuiling Ding. By using the commercial ruthenium-MACHO pincer complex, they achieved catalyst TONs up to 87000 for hydrogenation cyclic carbonates, which is about one order of magnitude higher compared to the direct conversion of carbon dioxide to methanol, underlining the possible advantage of this indirect CO_2 reduction route.[31] Apart from expensive precious metal complexes, the first non-noble metal catalysts for this transformation were reported only very recently. In 2018, the groups of Leitner,[32] Rueping[33] and Milstein[34] at the same time reported manganese pincer complexes for the hydrogenation of organic carbonates under basic conditions.



Scheme 1: Overview of selected reported homogeneous systems for the hydrogenation of organic carbonates to the corresponding alcohols.

[a] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany
[b] Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy
[c] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy
[d] Qatar Environment and Energy Research Institute (QEERI), Hamad bin Khalifa University (HBKU), Qatar Foundation, Doha, Qatar

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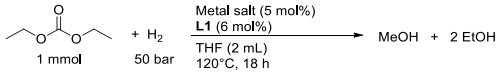
Modifying a system based on the combination of cobalt and Triphos, initially reported by Elsevier and de Bruin for the reduction of carboxylic acid, [35] our group succeeded in the direct hydrogenation of carbon dioxide with a homogeneous cobalt catalyst.[19] Later on, improved results have been obtained by us,[20] as well as by Klankermayer and Schieweck.[7] To the best of our knowledge, the applicability of such complexes for reduction of organic carbonates has not been reported yet. In this context, herein we describe the efficient hydrogenation of cyclic and acyclic carbonates in 2,2,2-trifluoroethanol (TFE) in the presence of $Co(BF_4)_2{\cdot}6H_2O$ and a modified Triphos ligand.

Results and Discussion

At the beginning of our investigations, different cobalt precursors in the presence of the ligand Triphos were tested for the hydrogenation of the model substrate diethyl carbonate at 120 °C and 50 bar H_2 (see

Table 1). Unfortunately, no active catalyst could be generated in the presence of coordinating anions such as halides (entries 1 and 2) acetyl acetonate (entries 3 and 4), carbonate and acetate (entries 6 and 7). Also the use of the cobalt hexafluoroacetylacetone did not show any appreciable yield of MeOH (entry 5). Finally, we found that $Co(NTf_2)_2$ and $Co(BF_4)_2{\cdot}6H_2O$ are both suitable for the hydrogenation of carbonates (entries 8 and 9), even at reduced catalyst loadings of 2 mol% (entries 10 and 11). $Co(NTf_2)_2$ afforded the highest conversions but a lower selectivity than $Co(BF_4)_2$. Although the use of $Co(NTf_2)_2$ gave good activities for CO_2 reduction,[20] here the low yield of alcohols is ascribed to the decomposition of the triflimide-anion which reacted with the substrate. In fact, we observed by GC-MS the formation of several unidentified by-products containing fragments derived both from diethyl carbonate and the NTf_2-anion.

Table 1: Testing different cobalt precursors for the hydrogenation of diethyl carbonate.

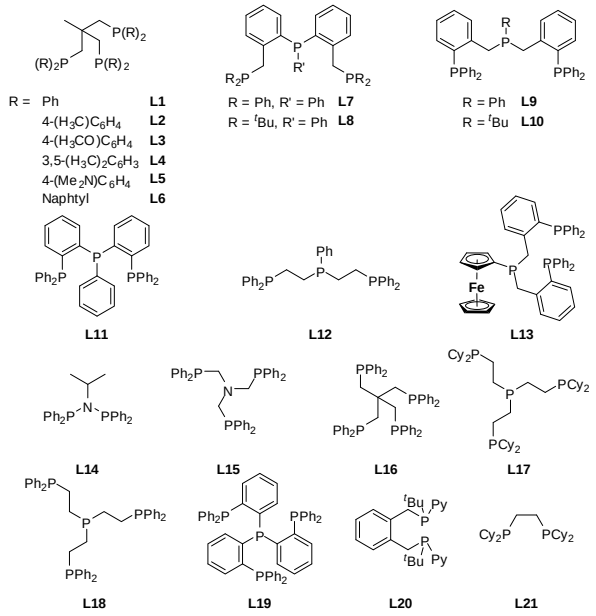


Entry	Co Precursor	Conversion [%]	Yield EtOH [%]	Yield MeOH [%]
1	$CoCl_2$	6	<1	<1
2	CoF_2	2	<1	<1
3	$Co(acac)_2$	4	<1	<1
4	$Co(acac)_3$	4	<1	<1
5	$Co(acac^F)_2$	2	<1	<1
6	$CoCO_3 \cdot 0.33\ H_2O$	1	<1	<1
7	$Co(OAc)_2$	3	<1	<1
8	$Co(NTf_2)_2$	60	37	13
9	$Co(BF_4)_2{\cdot}6H_2O$	36	31	25
10[a]	$Co(NTf_2)_2$	44	36	8
11[a]	$Co(BF_4)_2{\cdot}6H_2O$	24	22	16

Reaction conditions: General conditions: 1.0 mmol diethyl carbonate, 2 mol% cobalt precursor, 2.4 mol% **L1**, 2 mL THF, 120 °C, 50 bar H_2, 18 h. Conversions and yields were calculated *via* GC using hexadecane as internal standard. $acac^F$ = hexafluoroacetylacetone. [a] Co precursor = 0.02 mmol (2 mol%), **L1** = 0.024 mmol.

After identifying an active catalyst system, we tried to improve the comparably low activity investigating different ligands in the presence of cobalt tetrafluoroborate hexahydrate. Here, a variety of bidentate (**L20** and **L21**), tridentate (**L1** – **L14**) and tetradentate ligands (**L15** – **L19**) was tried. Similar to Co-catalysed hydrogenation reactions of carboxylic compounds, also in the case of carbonates solely ligands with the Triphos backbone were suitable. All the other ligands tested gave only traces of methanol and ethanol.

Table 2: Hydrogenation of diethyl carbonate: Variation of ligands in combination with $Co(BF_4)_2{\cdot}6H_2O$.

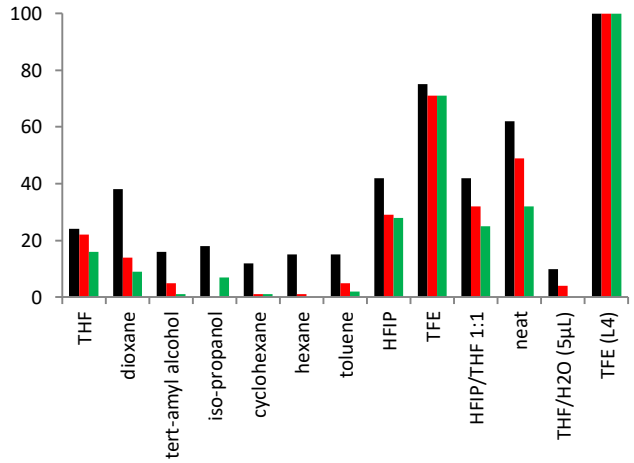


Entry	Ligand	Conversion [%]	Yield (EtOH) [%]	Yield (MeOH) [%]
1	**L1**	24	22	16
2	**L2**	37	32	26
3	**L3**	45	37	32
4	**L4**	57	48	42
5	**L5**	30	27	22
6	**L6**	4	<1	0
7	**L7**	4	<1	<1
8	**L8**	19	<1	<1
9	**L9**	29	<1	<1
10	**L10**	32	1	<1
11	**L11**	17	<1	0
12	**L12**	6	<1	<1
13	**L13**	5	1	<1
14	**L14**	4	<1	<1
15	**L15**	6	<1	<1
16	**L16**	2	<1	<1
17	**L17**	4	<1	0
18	**L18**	3	<1	0
19	**L19**	11	<1	0
20	**L20**	6	<1	0
21	**L21**	3	<1	<1
22	no ligand	4	<1	<1

General conditions: 1.0 mmol diethyl carbonate, 2 mol% $Co(BF_4)_2{\cdot}6H_2O$, 2.4 mol% ligand, 2 mL THF, 120 °C, 50 bar H_2, 18 h. Conversions and yields were calculated *via* GC using hexadecane as internal standard.

Among the Triphos-type ligands, the xylyl-Triphos **L4** revealed the highest productivity, followed by anisyl- (**L3**) and *p*-tolyl-Triphos (**L2**). The dimethylamino-substituted Triphos **L5** showed a slightly better productivity than **L1**. Thus, the substitution of the phenyl ring of Triphos with electron-donating groups seems to be beneficial for the system activity. However, the results are difficult to rationalize only on the

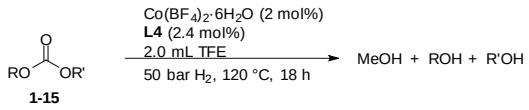
base of the basicity of the phosphorus. The catalytic behaviour can be better explained taking into account the steric properties of the ligands. Indeed, Leitner and Klankermayer recently showed the benefit of using sterically hindered ligands by comparing the activity of **L1**, **L2** and **L4** in the ruthenium/triphos-catalysed hydrogenation of methyl benzoate and lactams. The increased activity in the order **L4** > **L2** > **L1** is ascribed to the suppression of inactive hydride bridged ruthenium dimers formation.[36] The same trend was not noticed when cobalt was used instead of ruthenium for either the reduction of CO_2[7, 20] or reductive transformation of carboxylic acids,[37] suggesting a negligible role of dimers in catalyst deactivation. On the other hand, $[(Triphos)_2Co_2(\mu\text{-}H_3)]^+$ was found inactive, in the absence of acid co-catalysts, for the synthesis of dimethoxymethane and methyl formate from CO_2.[7] Considering the absence of additives in the present system, the prevention of dimer formation is a possible explanation for the order of activity of the ligands.

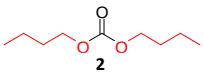
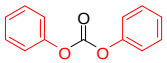
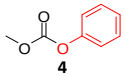
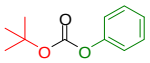
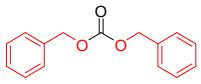
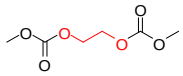
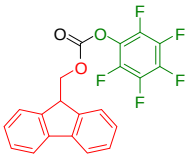
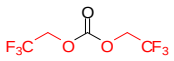
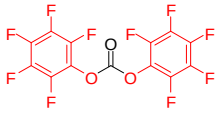
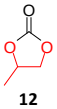


Scheme 2: Hydrogenation of diethyl carbonate: Solvent screening.
Reaction conditions: 1.0 mmol diethyl carbonate, 2 mol% $Co(BF_4)_2{\cdot}6H_2O$, 2.4 mol% **L1** or **L4,** 2 mL solvent, 120 °C, 50 bar H_2, 18 h. Conversions and yields were calculated *via* GC using hexadecane as internal standard. The ethanol yield could not be determined in the case of isopropanol as solvent.

Next, the performance of the in situ-generated catalyst with commercial ligand **L1** has been investigated in different solvents (Scheme 2). By far the best results were obtained with 2,2,2-trifluoroethanol (TFE) leading to 71% yield of both methanol and ethanol (conversion: 75%). Quantitative conversion and GC-yields for both alcohols have been achieved by combining the best solvent with the best ligand, **L4**. Previously, such beneficial effect of fluorinated solvents has been observed by Elsevier,[38] as well as by Klankermayer.[7] Interestingly, TFE gave significantly better results compared to the related solvent 1,1,1,3,3,3-hexafluoro isopropanol (HFIP). THF showed the best productivity as a non-fluorinated solvent. The sensitivity of the system towards water was shown by combining THF with 5 µL (0.28 mmol) of distilled water. Adding this small amount dropped the conversion from 24% to 10% and the yield of ethanol from 22% to 4%. Methanol formation could not be observed anymore. All other solvents resulted in low conversions, yields and selectivities. With an optimised system in hand, the hydrogenation of different organic carbonates was investigated in more detail (Table 3).

Table 3: Hydrogenation of carbonates to the corresponding alcohols: Substrate scope

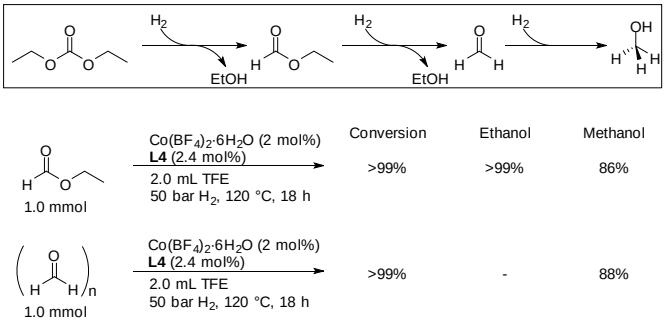


Entry	Substrate	Conv. [%]	MeOH [%]	ROH [%]	R'OH [%]
1	 **1**	>99	85	-	-
2	 **2**	>99	98	>99	-
3	 **3**	92	96	73	-
4	 **4**	>99	>99	>99	-
5	 **5**	94	84	n.d.[a]	89
6	 **6**	>99	11	88	-
7	 **7**	>99	94	54	-
8	 **8**	>99	92	97	91
9	 **9**	>99	80	n.d.[a]	-
10	 **10**	53	5	43	-
11	 **11**	>99	85	75	-
12	 **12**	>99	96	90	-

Reaction conditions: 1.0 mmol diethyl carbonate, 2 mol% $Co(BF_4)_2{\cdot}6H_2O$, 2.4 mol% **L4**, 2 mL TFE, 120 °C, 50 bar H_2, 18 h. Conversions and yields were calculated *via* GC using hexadecane as internal standard. When R = R', yields are reported as 2 ROH. [a] The peak of ROH overlaps with the one of TFE in the gas-chromatogram.

Dimethyl carbonate **1** gave three equivalents of methanol in a yield of 85% at full conversion. Almost quantitative yields of both alcohols have been achieved for di-*n*-butyl carbonate **2**. Also the aromatic carbonate **3** was effectively converted to methanol and phenol. The asymmetric aromatic/aliphatic carbonates **4** and **5** yielded the three corresponding alcohols. For dibenzyl carbonate **6**, a low methanol yield (11%) was

observed, even though the conversion and the yield of benzylic alcohol both have been high (<99%/88%). A similar behaviour was found for the perfluorinated carbonate **10**, although at a lower conversion. It is worth noticing that the used cobalt source contains six equivalents of water and both benzyl alcohol and pentafluorophenol are good leaving groups. Thus, for **6** and **10** hydrolysis of the substrates would lead to formation of alcohol, carbon dioxide. This, at least in part, accounts for the discrepancy of methanol and alcohol yields. The asymmetric carbonate **8**, which bears one hexafluorophenol unit yielded in 92% of methanol, along with 97% of 9-fluorenyl methanol and 91% of hexafluorophenol. Also the fluorinated substrate **9** was converted to methanol in high yield. Noteworthy, also the cyclic carbonates **12** and **13** were readily transformed to the diols and methanol. These carbonates are of particular interest *vide supra*, as they are commercially produced from carbon dioxide and epoxides or oxetanes.[39]



Scheme 3: Hydrogenation of the potential intermediates ethyl formate and formaldehyde.

As the hydrogenation of diethyl carbonate potentially occurs stepwise *via* ethyl formate and/or formaldehyde, these compounds have been investigated in separate hydrogenation experiments (Scheme 3). Both, ethyl formate and para-formaldehyde were completely hydrogenated, giving methanol in 86% and 88%, respectively, and ethanol in >99%. Therefore, although only traces of ethyl formate were detected by GC for the model substrate, we cannot exclude that these compounds indeed are intermediates in the hydrogenation of diethyl carbonate.

Conclusions

In conclusion, we investigated the homogeneous cobalt-catalysed hydrogenation of organic carbonates for the first time. The combination of $Co(BF_4)_2{\cdot}6H_2O$ with a Triphos-derived ligand **L4** resulted in an active catalytic system suitable for reduction of both cyclic and acyclic carbonates. At relatively mild conditions, good to very good yields of methanol and the corresponding alcohols have been obtained using the solvent TFE.

Experimental Section

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Materials

All chemicals were purchased from commercial sources and were used as received without additional purification, if not stated otherwise. Molecular hydrogen was purchased from Linde. All experiments were carried out under argon atmosphere by using standard Schlenk-techniques, unless stated otherwise. Solvents were dried and distilled or directly used from a solvent purification system (MBraun). THF was stored over molecular sieves 3 Å. Diethyl carbonate was distilled prior to use. The ligands **L2** – **L6**,[37] **L7** – **L9**,[40] **L11**,[40] **L15**,[41] **L16**,[42] **L17**,[43] **L19**,[44] and **L20**[45] have been synthesised according to literature-reported procedures.

Catalytic experiments were conducted in 4 mL screw cap vials, closed with a polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere by a needle, inside a 300 mL Parr autoclave and stirred with a magnetic stirring bar. GC measurements were carried out on a 7890A GC-System with HP-5 column (polydimethylsiloxane with 5% phenyl groups, length 30 m, i.d. 0.32 mm, film 0.25 µm) and with a FID coupled with a 7693 autosampler from Agilent Technologies. Argon was used as carrier gas. GC-analyses for methanol quantification were performed on an Agilent HP-6890 chromatograph with a FID detector and an Agilent HP Ultra 1 column (19091A-105, 50 m, 0.20mm i.d., 0.33 mm film thickness, 100% dimethylpolysiloxane) using argon as carrier gas.

In a typical catalytic experiment, $Co(BF_4)_2{\cdot}6H_2O$ (6.81 mg, 2.0 mmol) and ligand (2.4 mmol) were fast weighed in the air and transferred into a 4 mL glass vial. If used, solid substrates were also weighed in the air and added into the vial. The vial was subsequently set under argon. 2.0 mL solvent were added and the mixture stirred for 5-10 min. Then, liquid substrates were added and the vials were placed in a metal plate inside a 300 mL autoclave. After closing, the reactor was pressurised with hydrogen (about 20 bar), which was released again. This procedure was carried out three times, after which 50 bar H_2 were introduced. The autoclave was then heated inside an aluminium block to 120 °C for 18 h. Afterwards the reaction was quenched with an ice-bath and the reactor vented. Hexadecane (30 µL) was added to the reaction as internal standard for GC, along with 2 mL THF. After proper mixing, GC was measured of the sample.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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